Oak Ridge National Laboratory

Ambient Temperature Polysulfide-Based Redox Flow Batteries and Membrane Development

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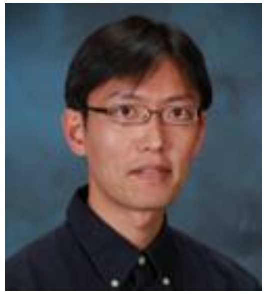

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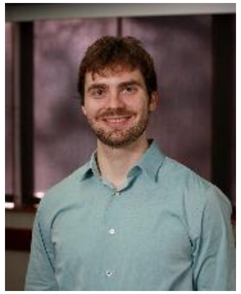

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Thrust Area : Cost competitive materials and systems for enabling Long Duration Energy Storage (LDES)

(i) Development and demonstration of high-performance electrochemical systems and components utilizing earth abundant materials
(ii) Research on novel materials and system components to resolve key cost and performance challenges for electrochemical energy storage systems meeting demands for grid-scale energy storage

Potential Use Case – Long Duration Energy Storage (10-100 Hrs. at rated power)

Long Term Goals and Requirements

- Reduce the cost of energy storage systems by 90% by the decade for 10+ hours of storage as per the
  DOE's Long Duration Storage Earth Shot
- Levelized cost of electricity (LCOS) at 5 cents/KWhr for long duration storage.
- Energy round trip efficiency (RTE) > 50%
- Provide multiple value streams : Enable several applications with a single, long operating-life asset

Project Metrics and Milestones

- Develop and test Na-polysulfide redox flow cell for long-duration energy storage
- Synthesize, fabricate, and optimize Na-ion based composite membranes
  - Targets: Na^+ conductivity > 10^{-4} S/cm; transference number t_+ > 0.7; Youngs modulus > 10 Mpa
  - Focus in FY21 –Developed single-ion conducting membranes from commercial Kraton Nexar ionomer.
- Test membranes in redox flow system to study durability and mitigate degradation of membranes and redox species.
  - Target: Membrane area specific resistance (ASR) < 100 ohm-cm^2
- Test compatibility and chemical crossover of membrane separators for Na-polysulfide catholytes versus Na-metal

Lab-scale prototypes were built to characterize sodium polysulfide-based catholytes for low-cost, high energy nonaqueous RFBs.

Experimental Details

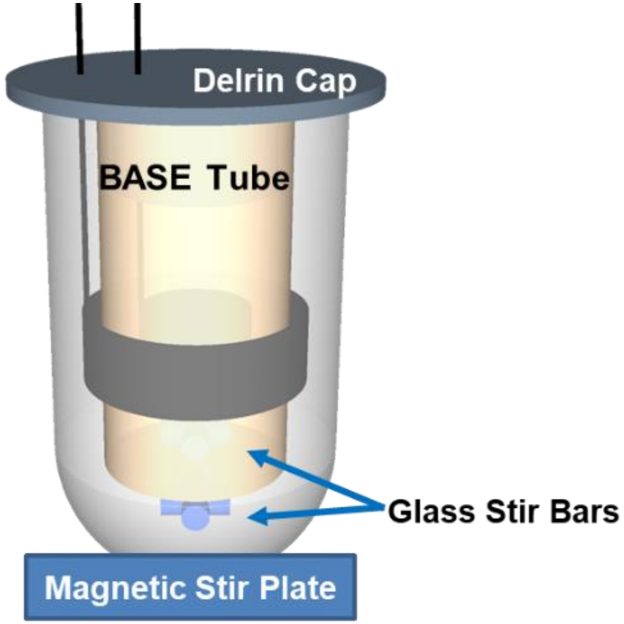
Supporting Electrolyte: 0.9 m NaTFS in diglyme
Membrane: $Na^{+}ß" Al_2O_3$ plate (BASE, 1mm thick)
Current Collectors: Nickel foam + Carbon felt

Cathode: $Na_2S_8 + 2\,Na^+ + 2\,e^- \leftrightarrow 2\,Na_2S_4$ $E^0 = 2.3$ V vs. Na/Na+

Anode: $Na^+ß^{\bullet -} \leftrightarrow ß^0 + Na^+ + e^-$ $E^0 = 0.2$ V vs. Na/Na+

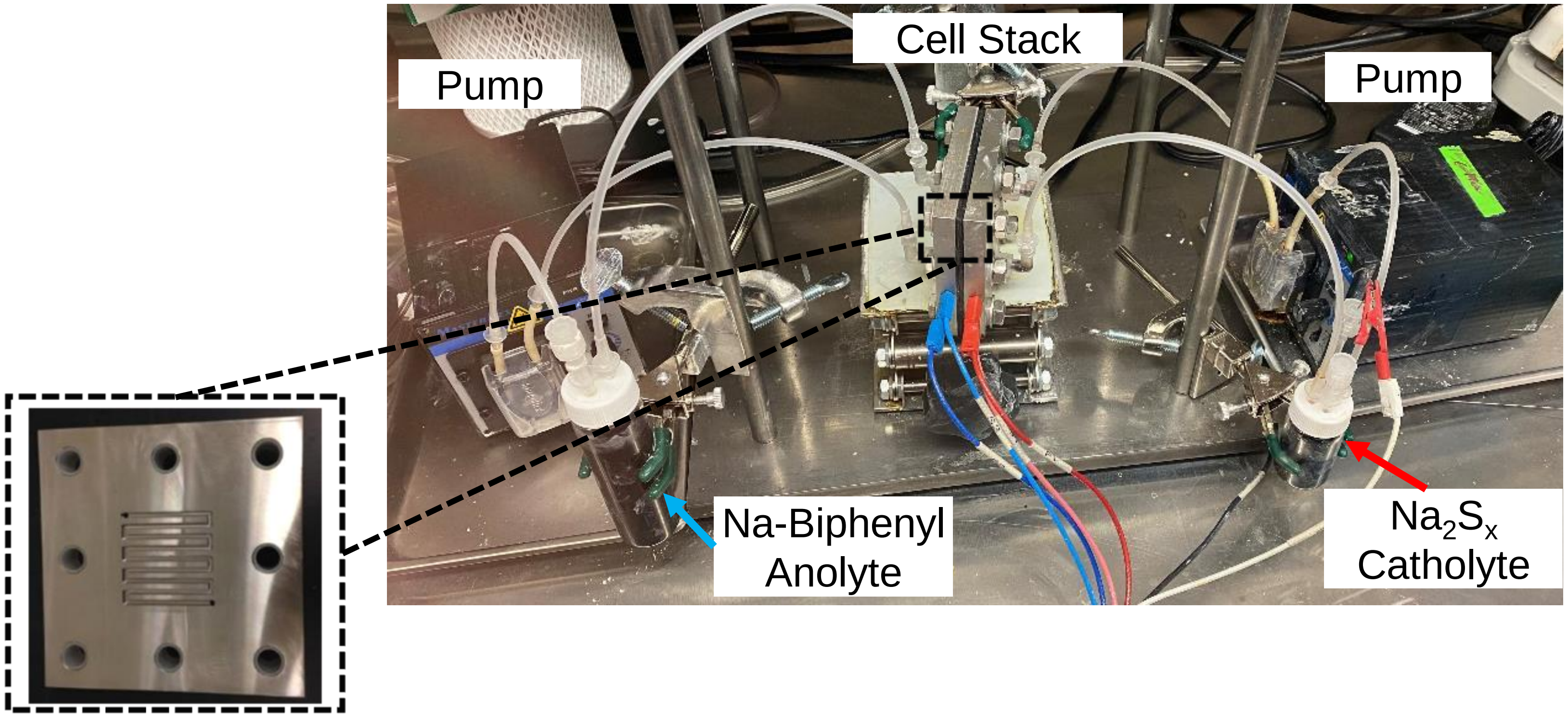
Full Cell: $Na_2S_8 + 2\,Na^+ß^{\bullet -} \leftrightarrow 2\,Na_2S_4 + 2\,ß^0$ $E_{cell} = 2.1$ V

Cylindrical Cell Configuration

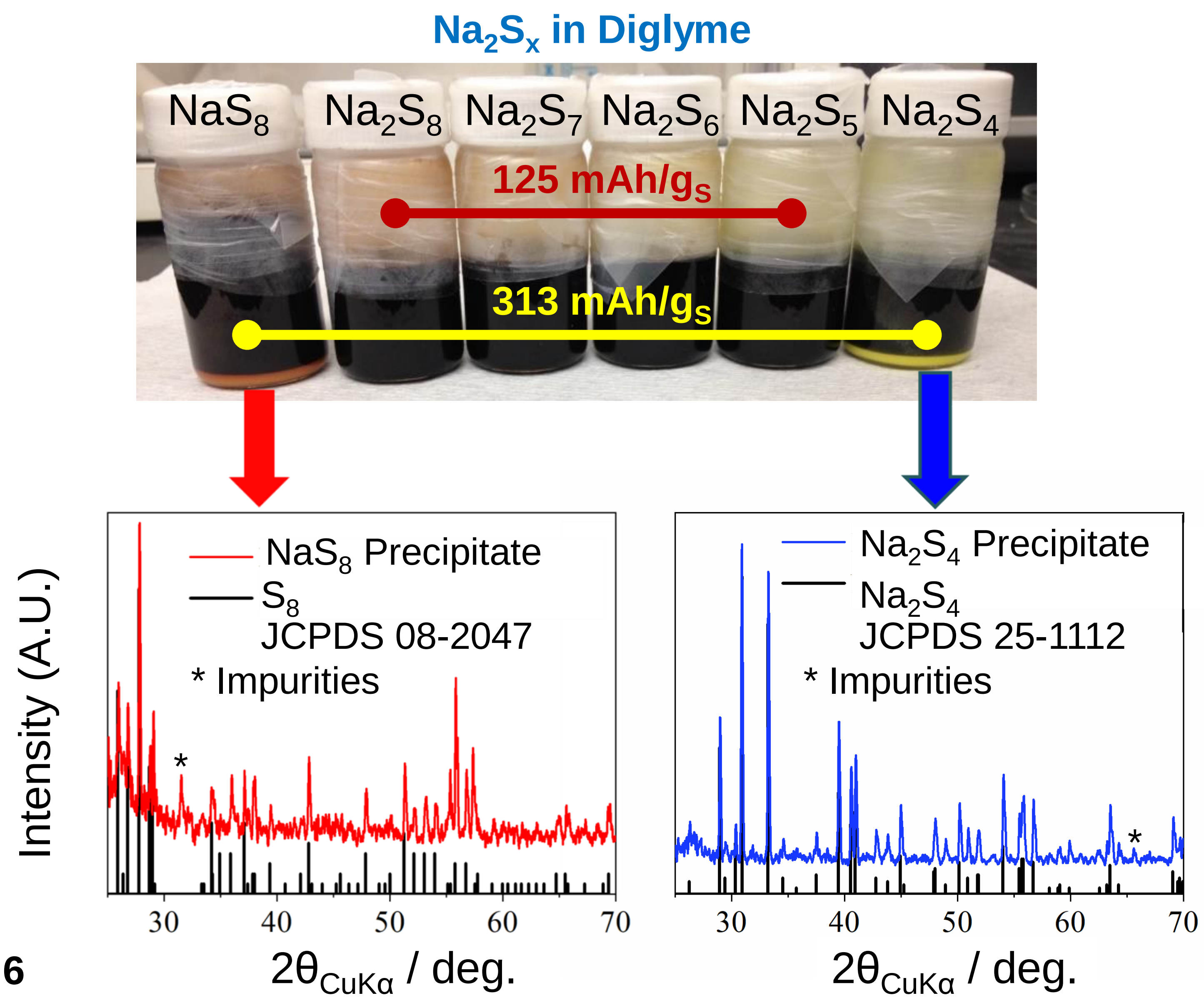


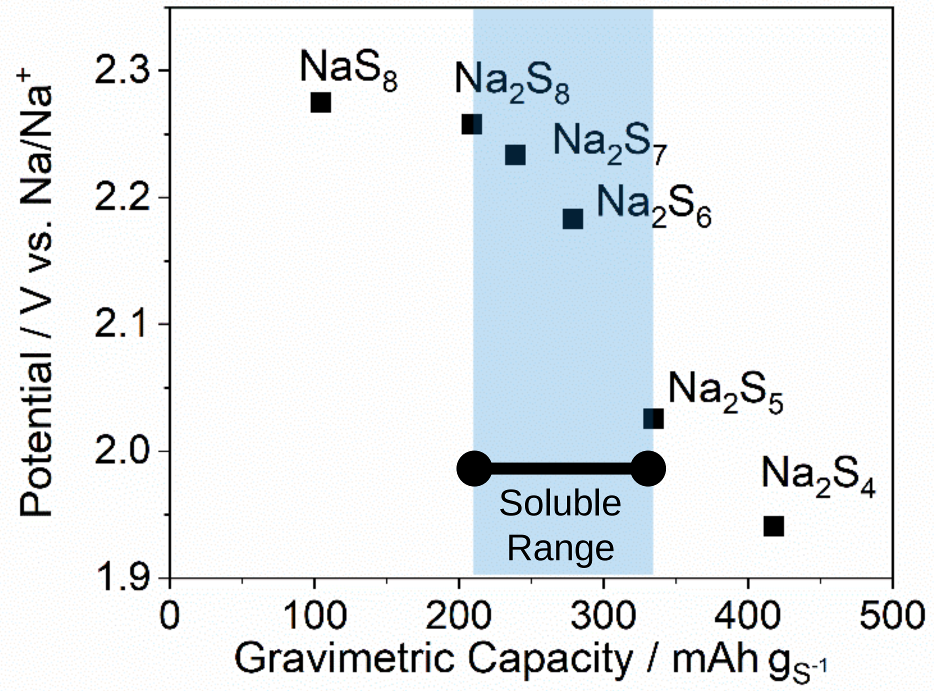
Inner: Na_2S_x Catholyte
Outer: Na-Biphenyl ($Na^+ß^{\bullet -}$) Anolyte

Flow Cell Configuration



Na_2S_x is highly soluble in diglyme when $5 \leq x \leq 8$. Outside this range, insoluble S and Na_2S_4 phases form which may impact flow battery performance.

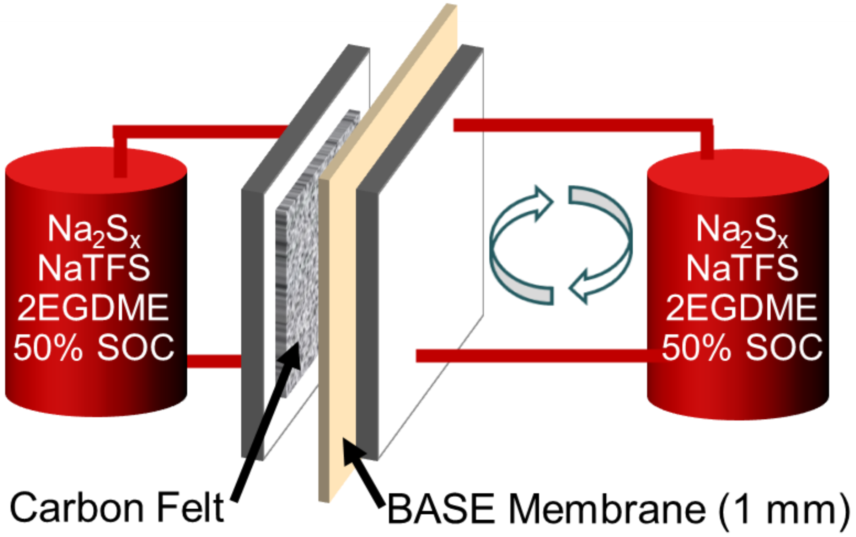




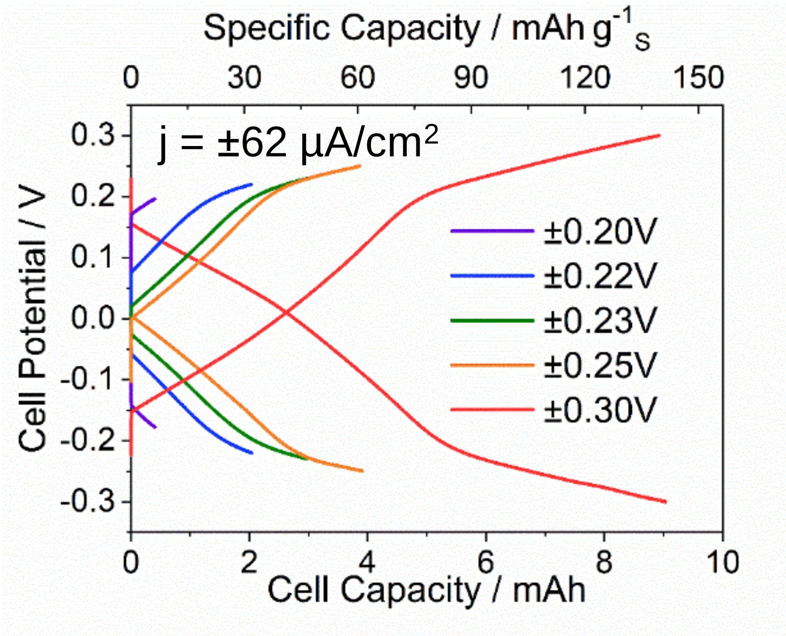
Primary Goals of Study

1. Assess reversibility of reactions involving soluble vs. insoluble Na_2S_x phases
2. Assemble and test lab-scale prototypes with biphenyl anolyte and Na_2S_x catholyte
3. Identify rate limiting processes in full cell prototypes.

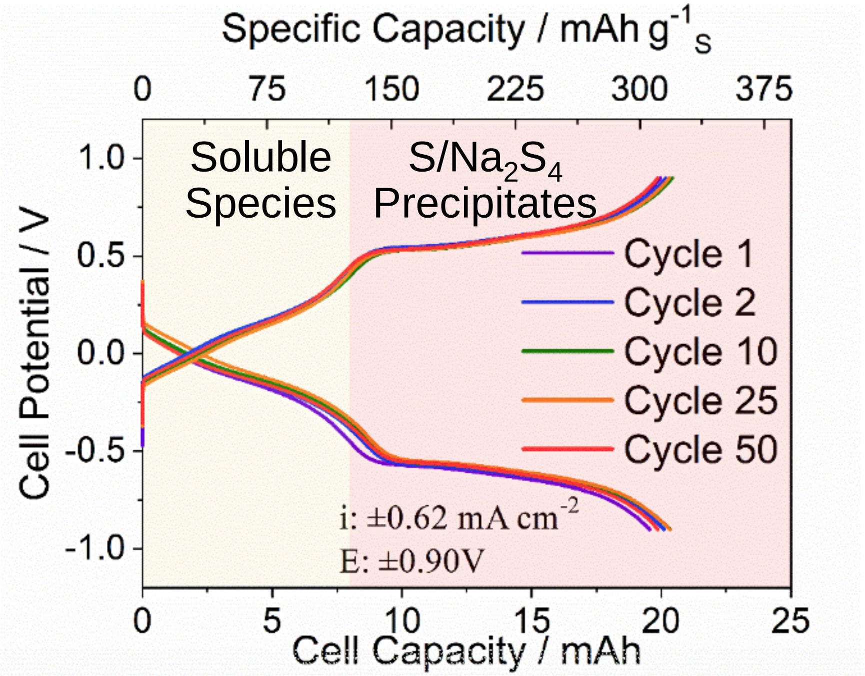
Forming insoluble products (S and Na_2S_4) in the stack does not inhibit reversibility. Symmetric RFBs exhibit outstanding cyclability and 100% coulombic efficiency within experimental error.

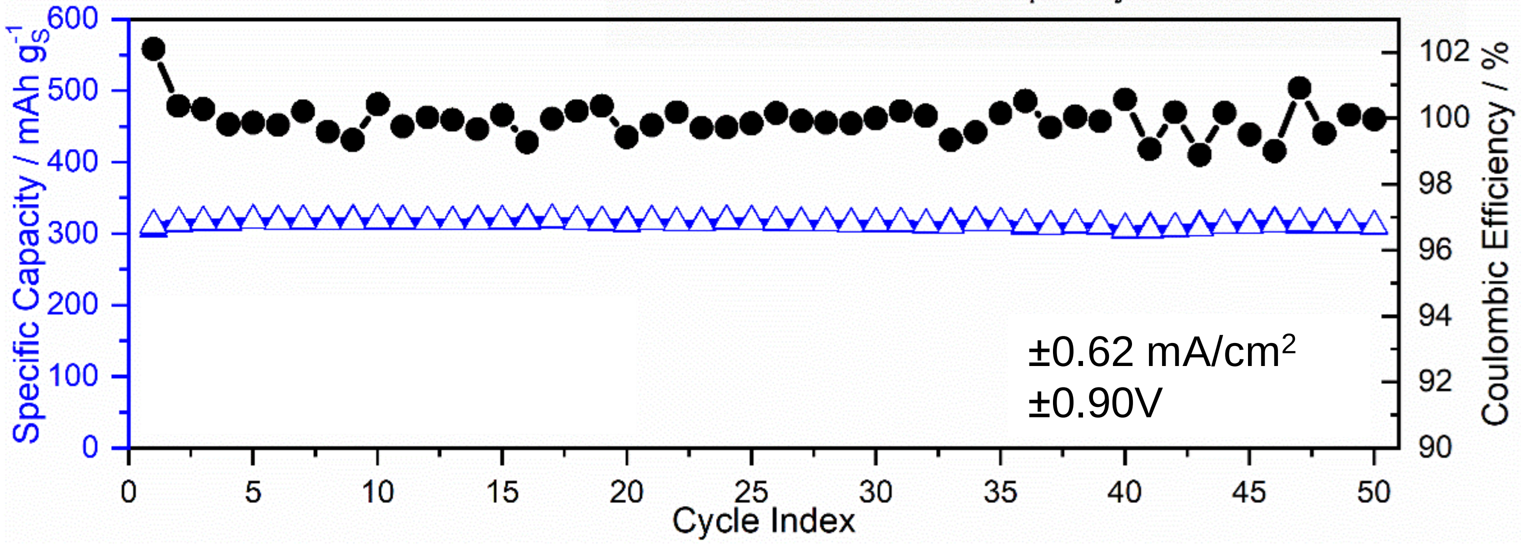


Cycling Soluble Phases ($Na_2S_8 \leftrightarrow Na_2S_5$)



Cycling Insoluble Phases (S ↔ Na_2S_4)

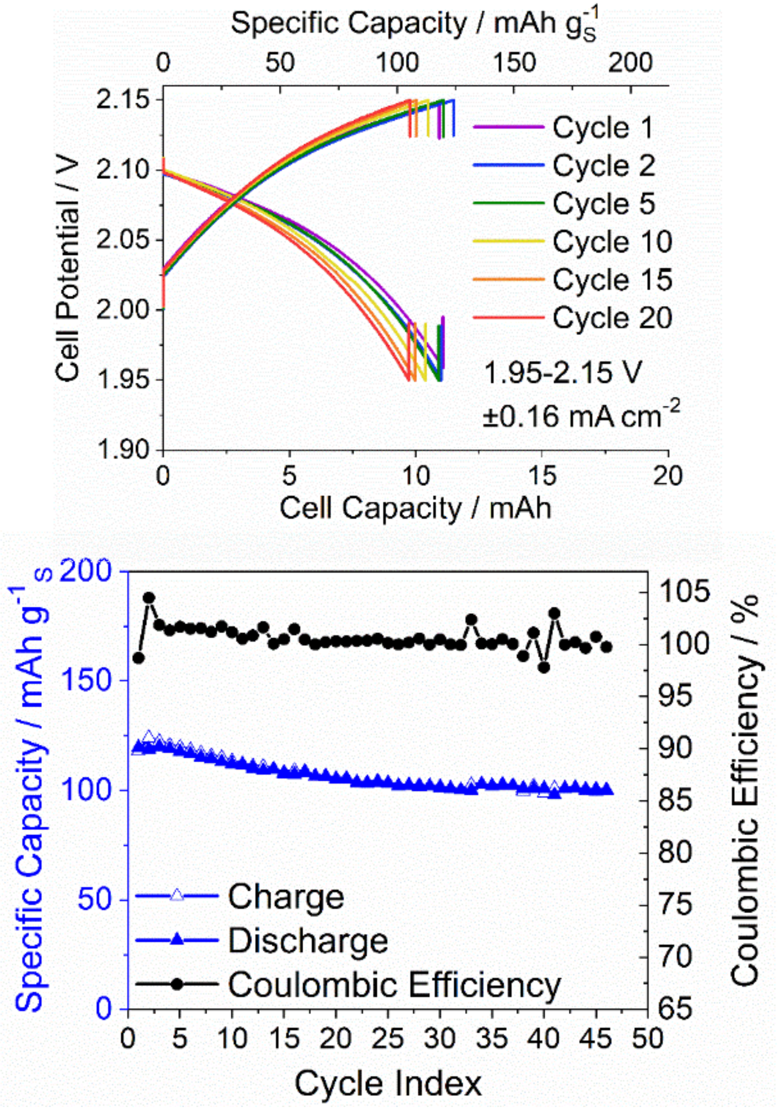




Nonaqueous biphenyl/Na_2S_x full cells exhibit outstanding cycling stability.

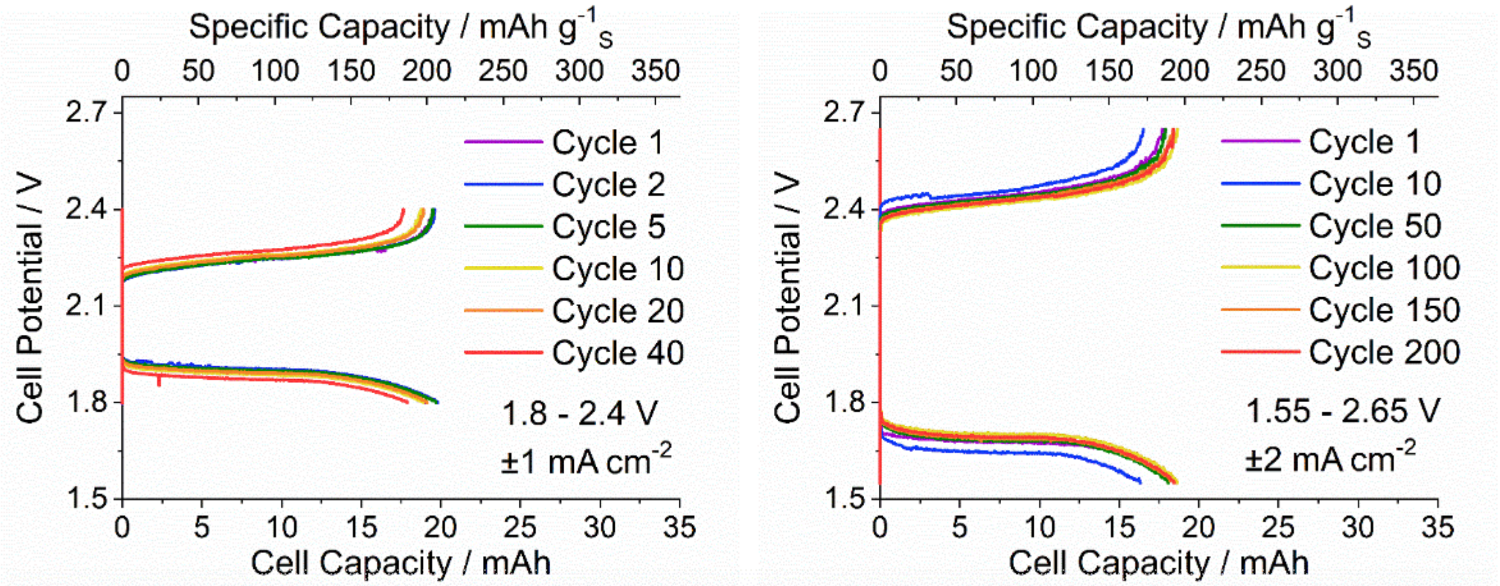
Full Cell: Cycling Soluble Phases

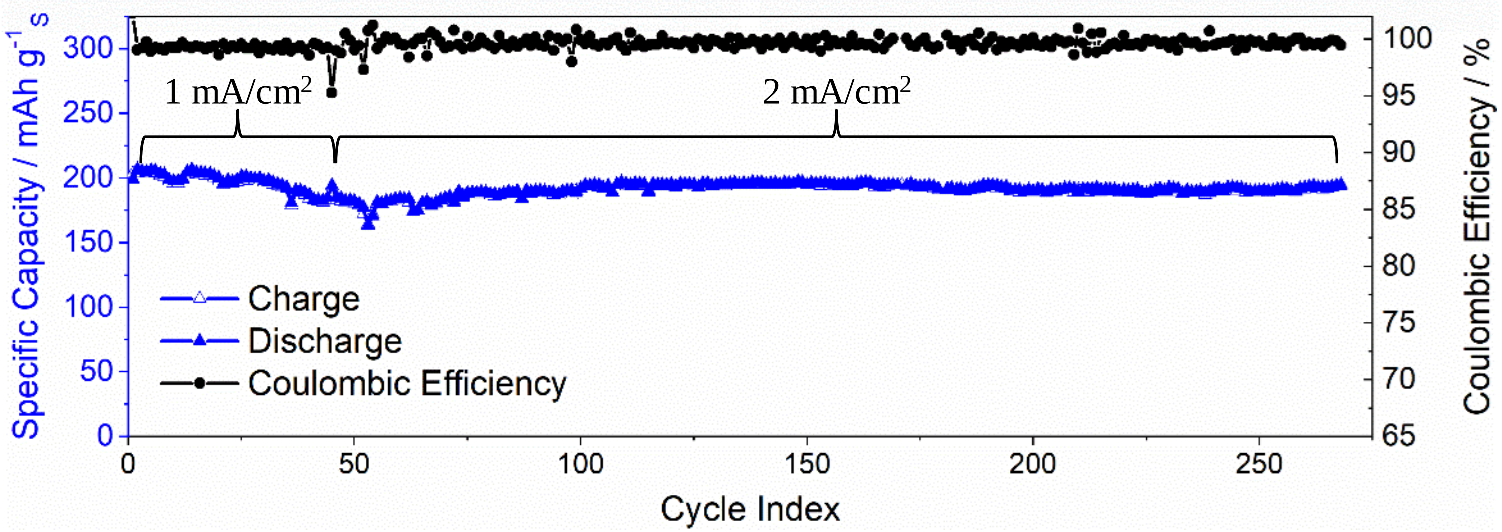
$Na_2S_5 \leftrightarrow Na_2S_8$ ($Q_{theoretical}$ = 125 mAh/g_S)



Full Cell: Cycling Insoluble Phases

$Na_2S_8 \leftrightarrow S_8$ ($Q_{theoretical}$ = 209 mAh/g_S)





3 electrode AC impedance measurements were performed to identify rate limiting processes in biphenyl/Na_2S_x RFBs. Voltage losses are dominated by processes at the cathode.

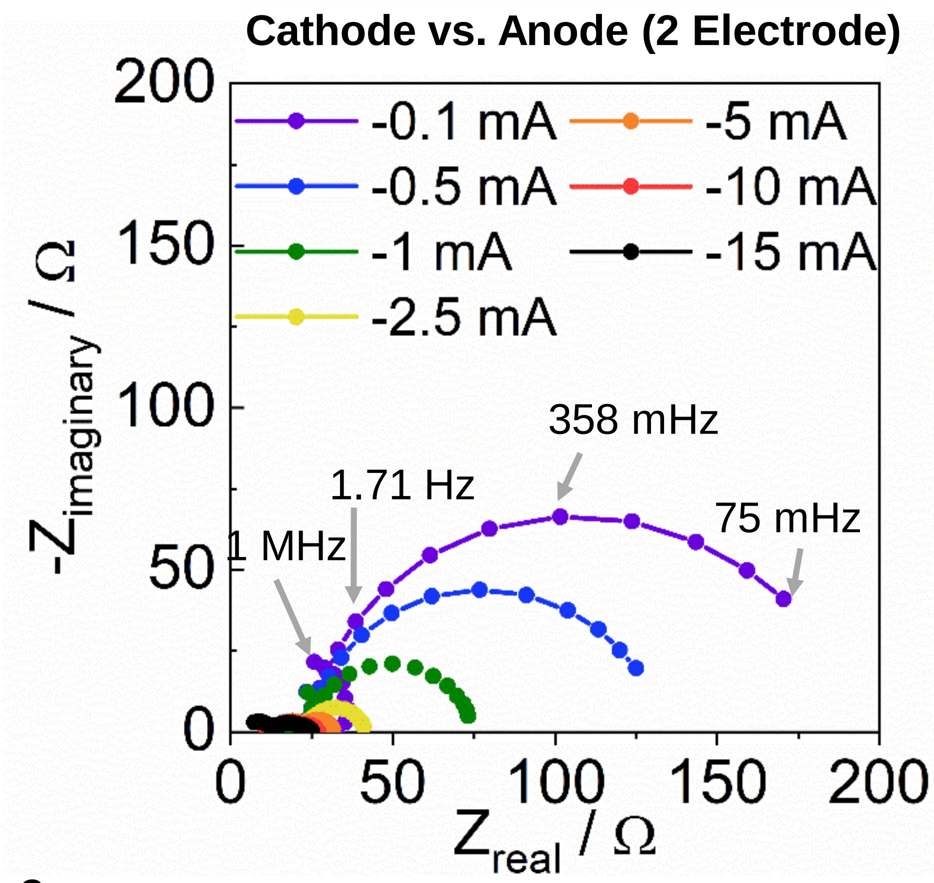
Approach

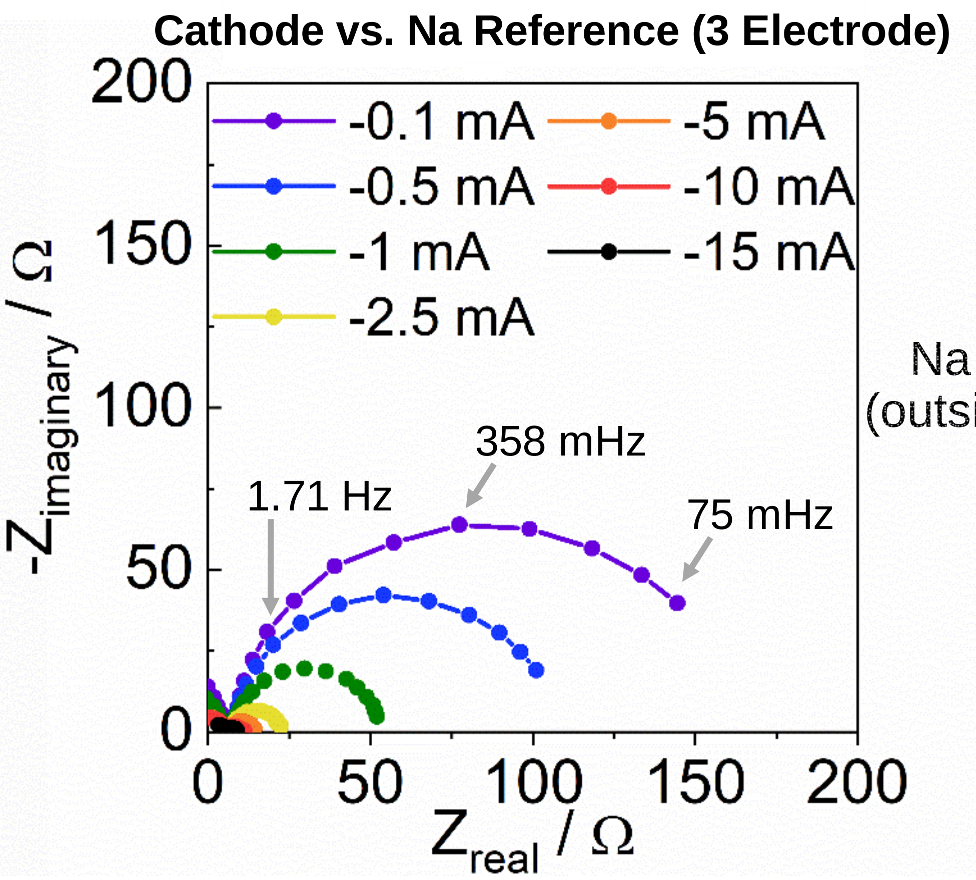
1. Apply i_{DC} + i_{AC} perturbation and measure E_{DC}/E_{AC} response (E_{AC} < 10 mV)
2. Z = dη/di describes **local** behavior

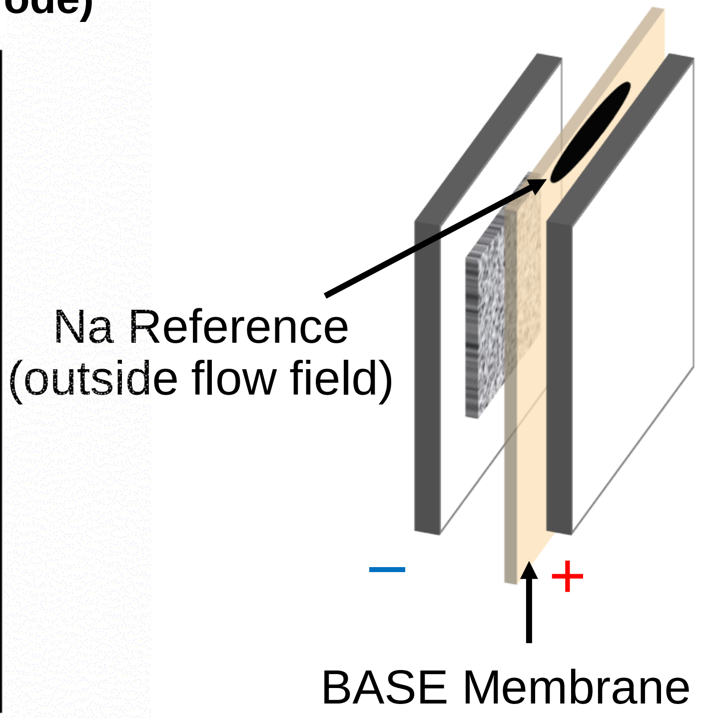
⇨ Integrate R_{hf} and R_{lf} to obtain **global** polarization relationships

$$\boxed{\eta_x(i) = \int_0^i Z_x(i')di'}$$

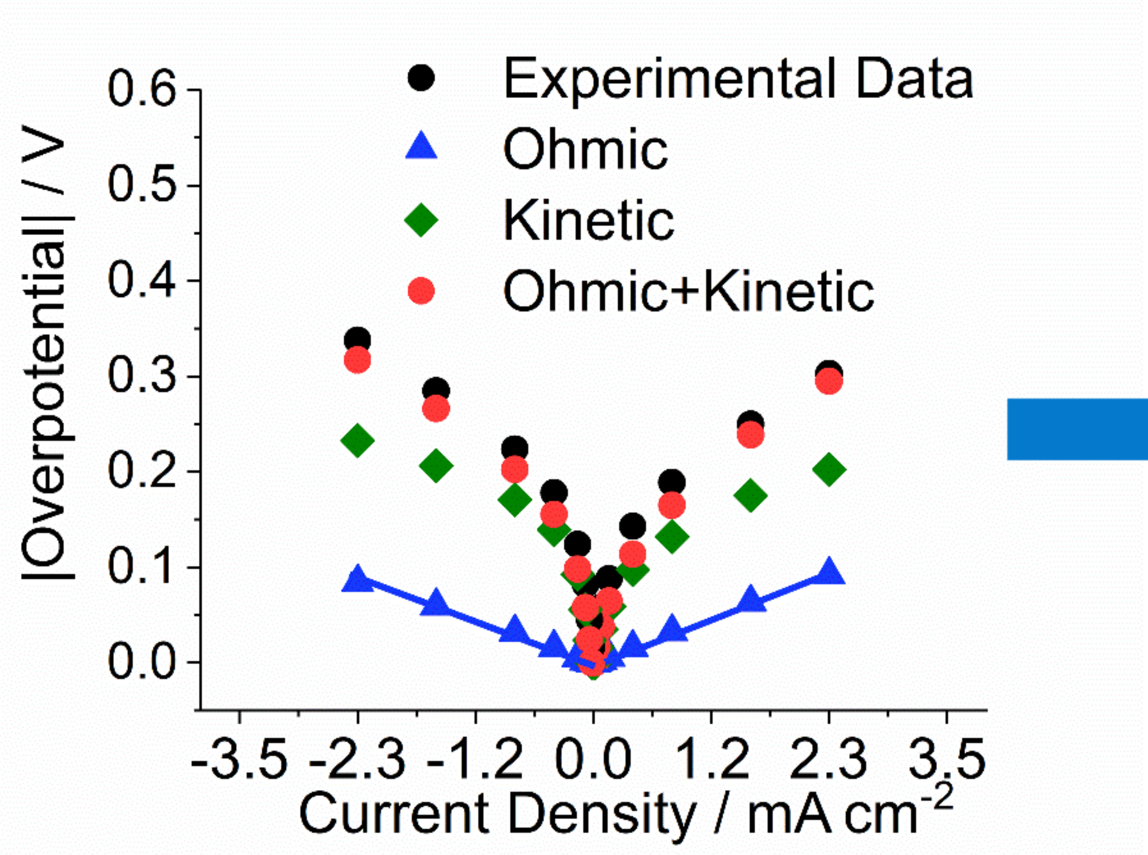
J. Electrochem. Soc. **2017**, 229(1), 261.

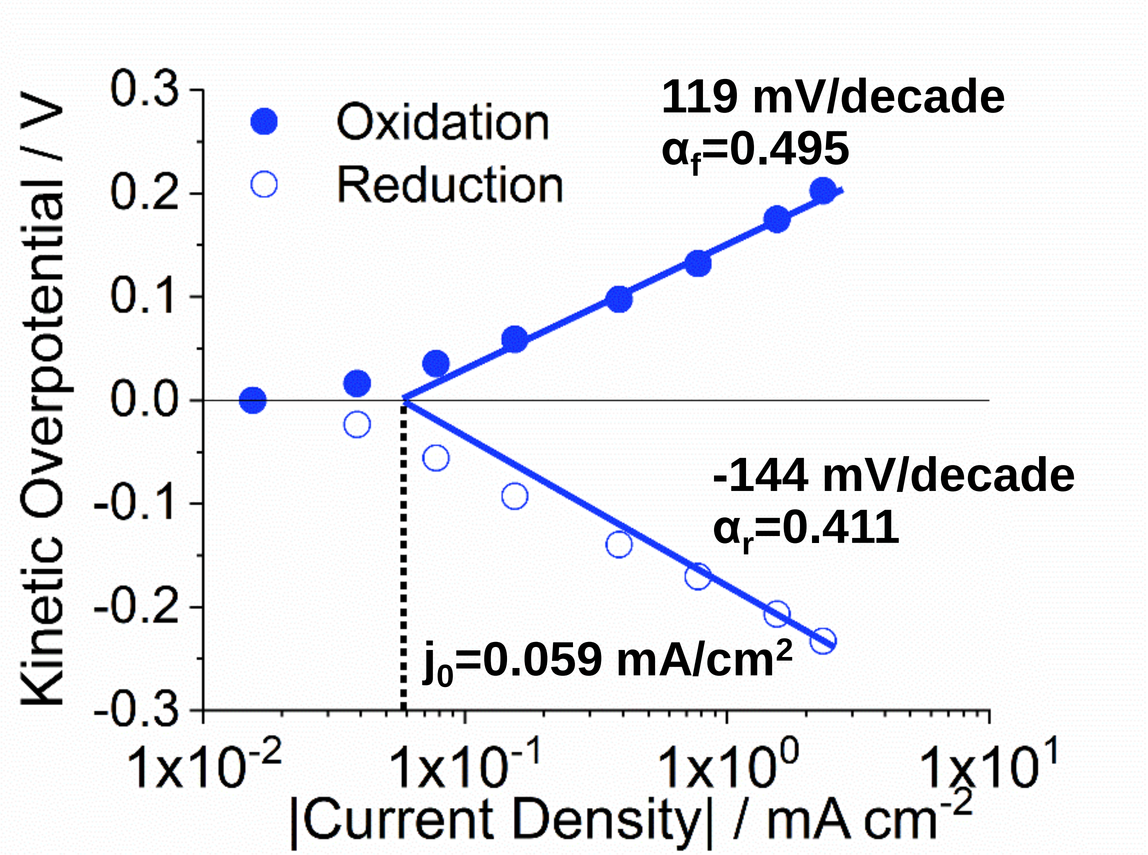






Numerical integration of impedance features enables quantification of voltage losses associated with ohmic vs. kinetic vs. transport processes.

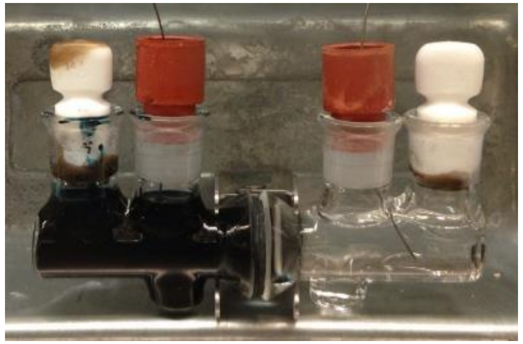




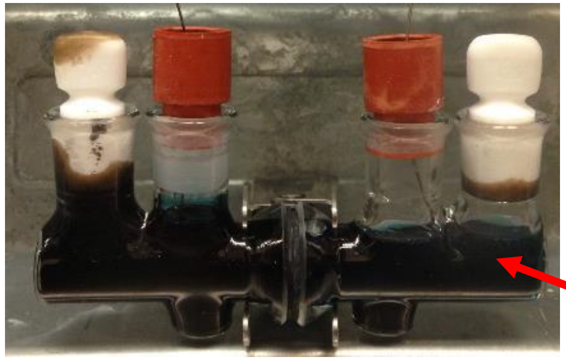
Key Conclusions

1. Voltage losses in biphenyl/Na_2S_x RFB are dominated by cathode reaction kinetics
2. Na_2S_x reaction is consistent with simple Butler-Volmer kinetic rate law
3. Concentration polarization was negligible over conditions investigated
4. AC impedance method demonstrated here can be used to guide component selection and system optimization

Polymer membranes are needed to replace BASE ceramics used in initial prototypes. Crossover of Na_2S_x through commercial polymer membranes was quantified using UV-vis.



Na_2S_x Crossover

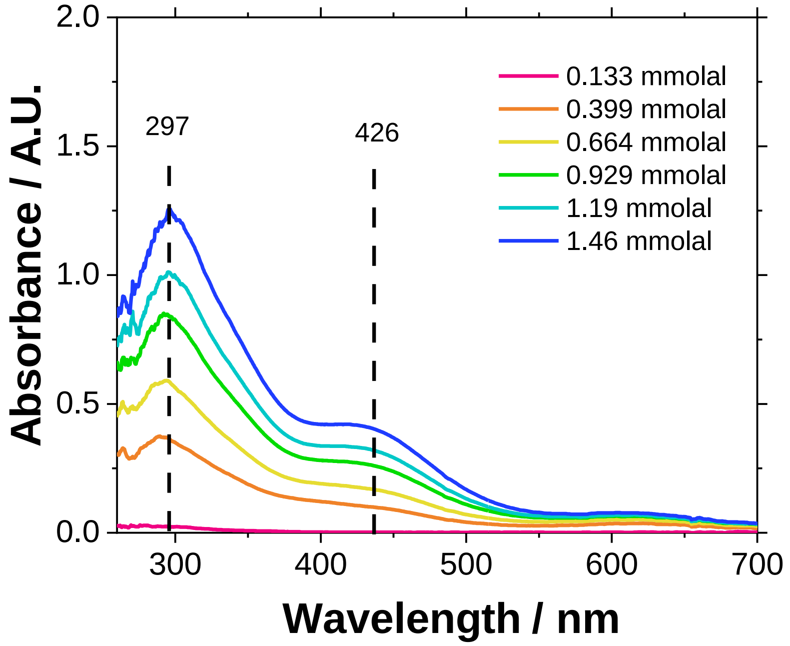


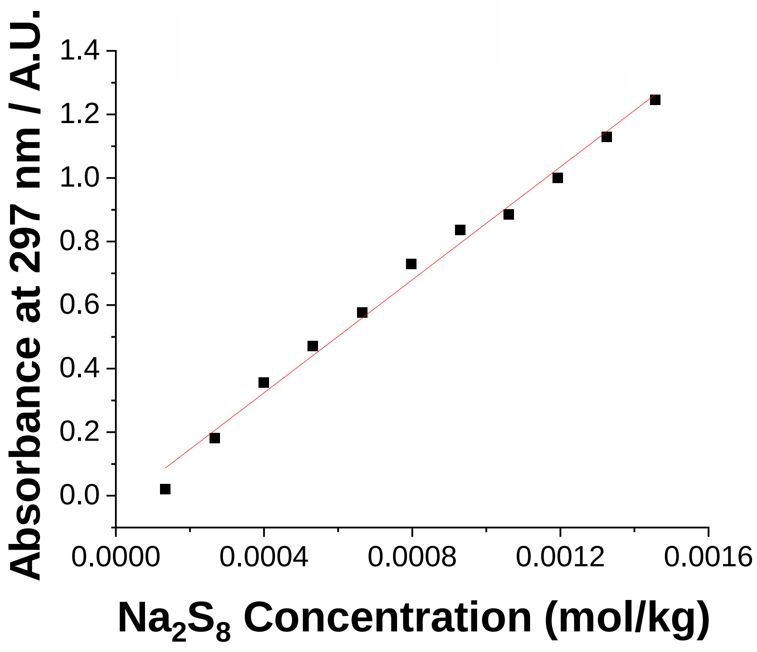
Commercial Polymer Membranes

1. Nafion 115 (Na^+ exchanged)
2. Celgard 2325 (microporous)

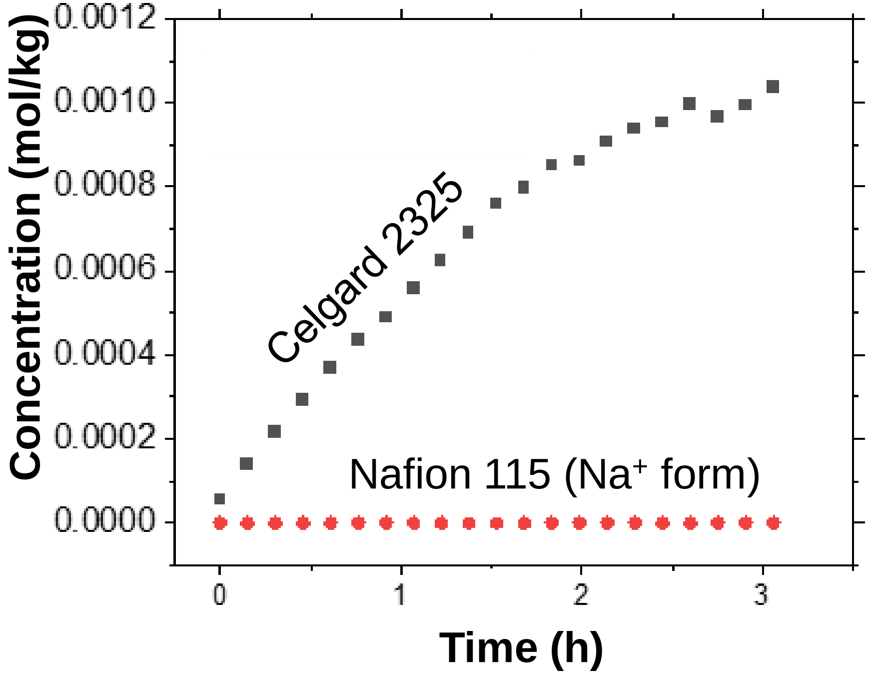
Measure $[Na_2S_8]$ in permeate as f(t) to quantify crossover rate

UV-Vis Calibration Curve for Na_2S_8



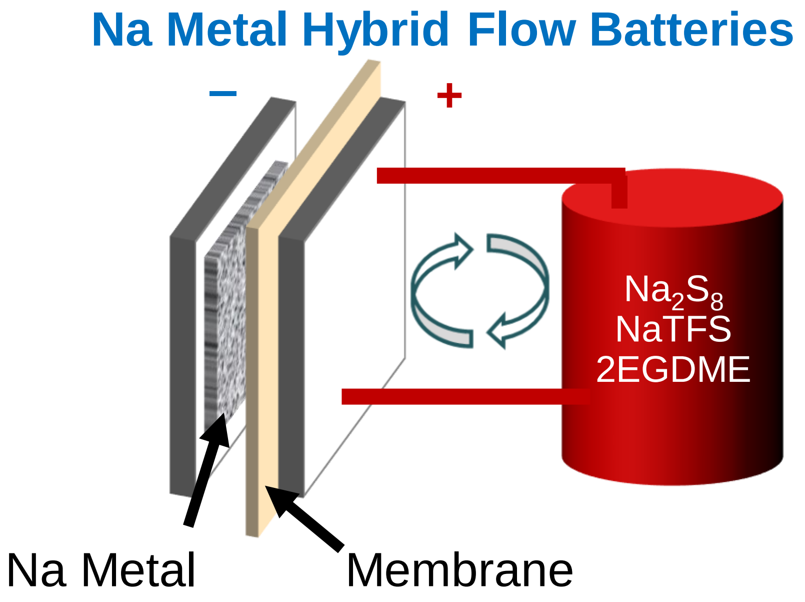


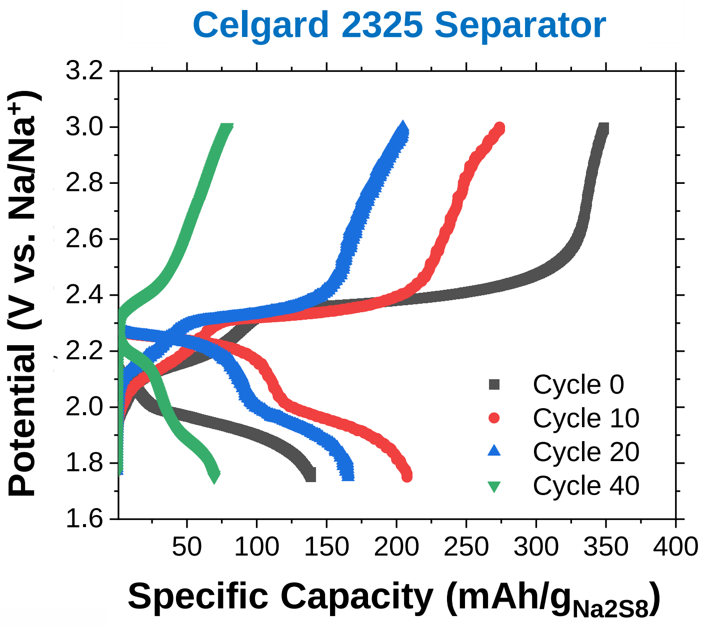
$[Na_2S_8]$ in Permeate

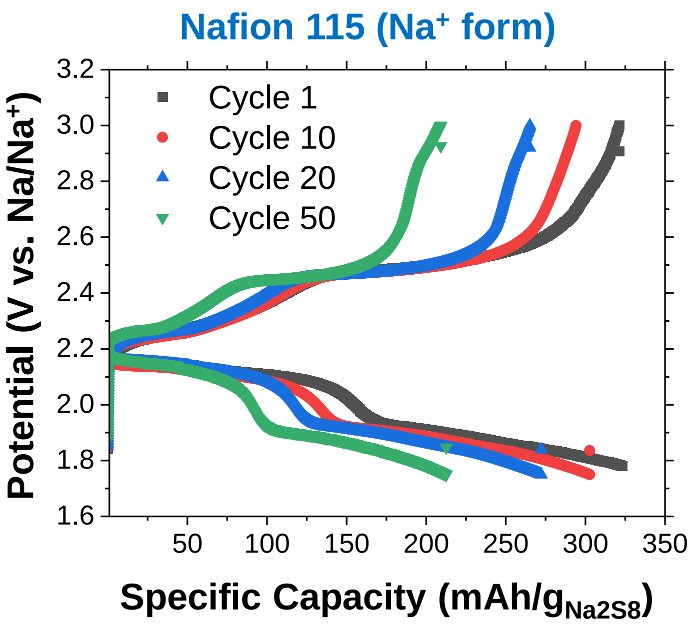


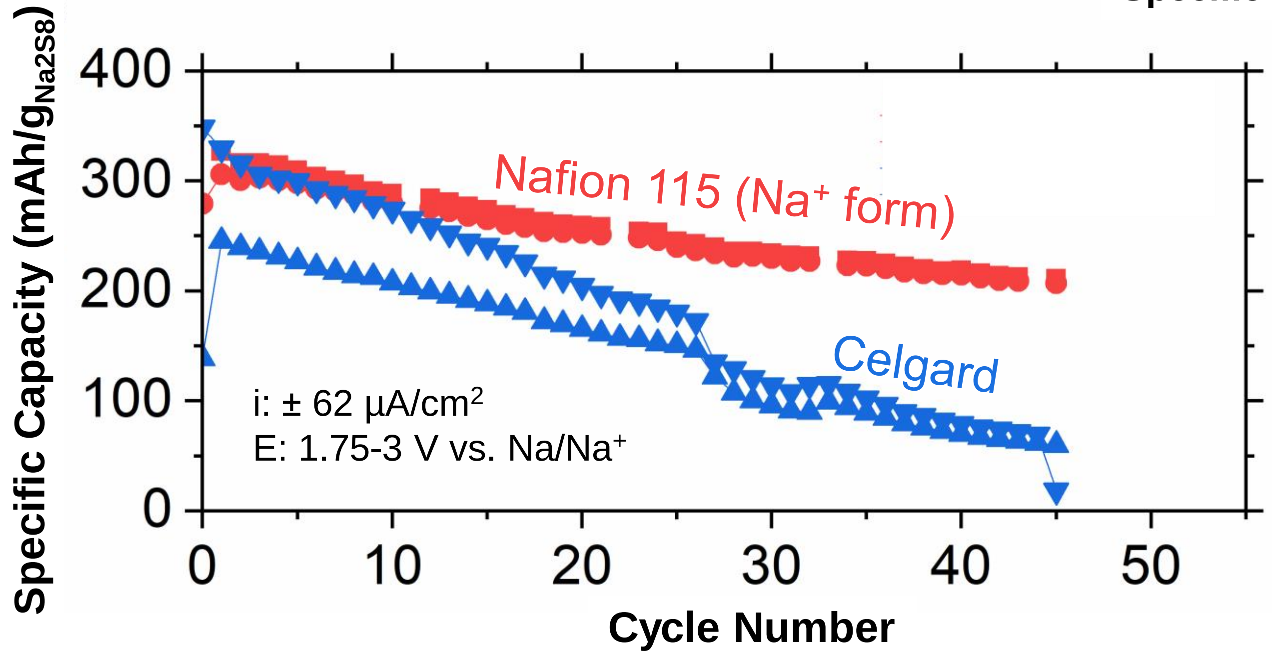
J. L. Tyler et al. **2022** (Unpublished)

The performance of commercial membranes was benchmarked in nonaqueous hybrid flow batteries containing Na metal anode and Na_2S_8 catholyte.









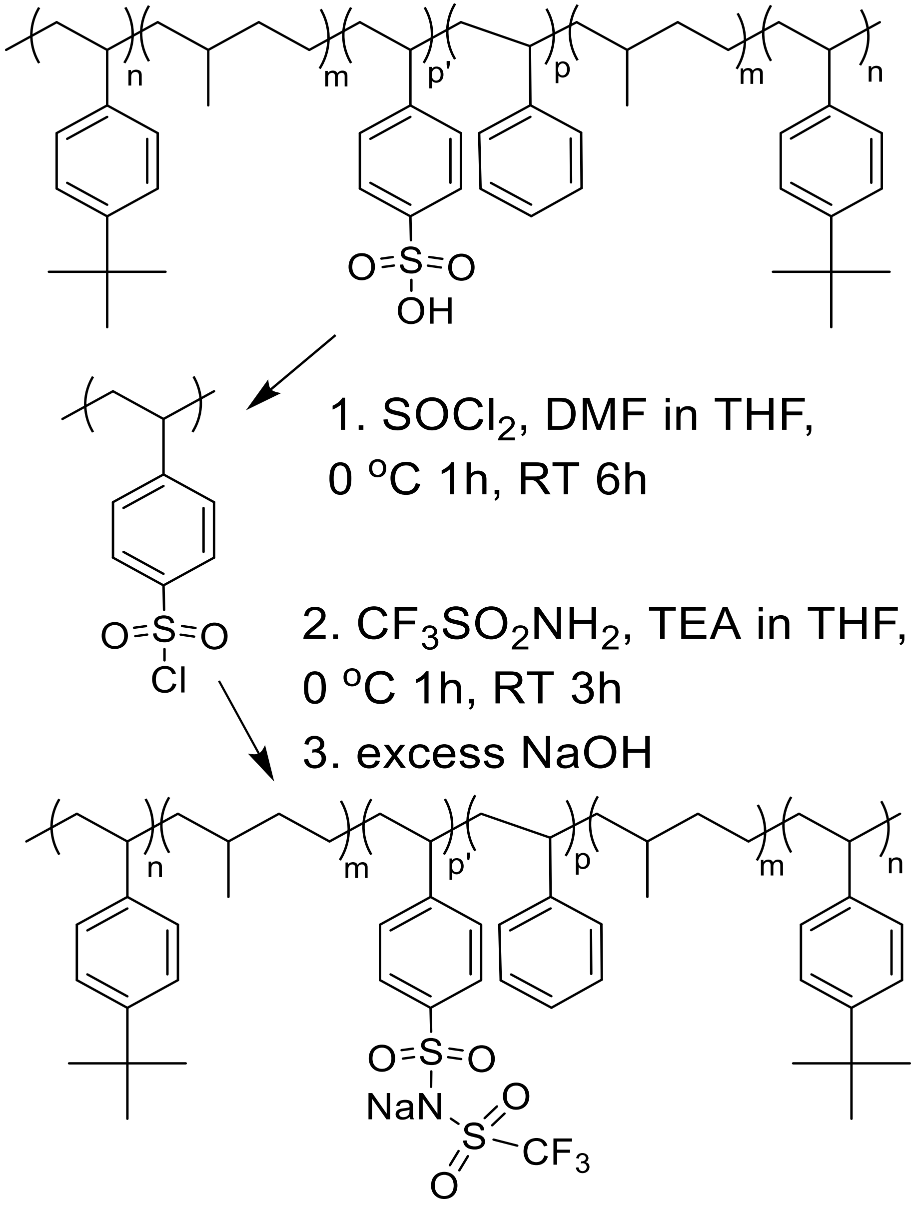
Key Findings:

1. Na_2S_x crossover through Celgard results in rapid capacity fade and low CE.
2. Hybrid Na|Nafion|Na_2S_8 hybrid flow cells exhibit high capacity and moderate cycling stability.
3. New polymer membranes are needed to mitigate capacity fade for long duration storage.

J. L. Tyler et al. **2022** (Unpublished)

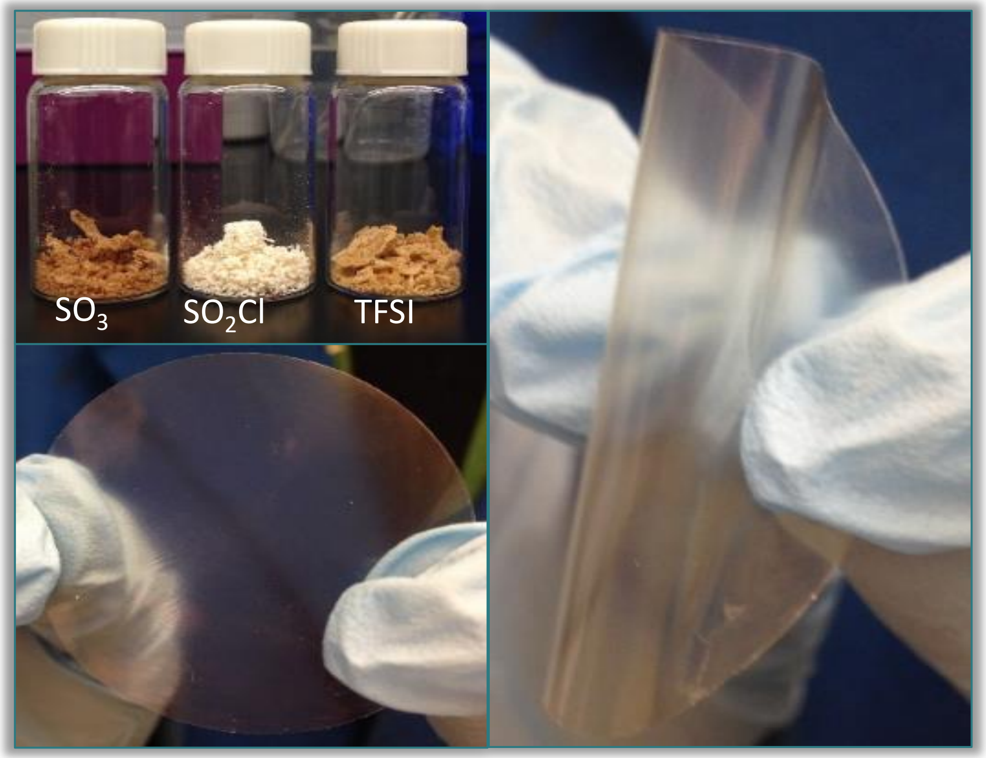
Single ion conducting membranes were developed by modifying a commercially available Kraton Nexar ionomer.

IEC 2.0 (H^+)



IEC 1.54 (Na^+)

- Conversion = at least 95 %

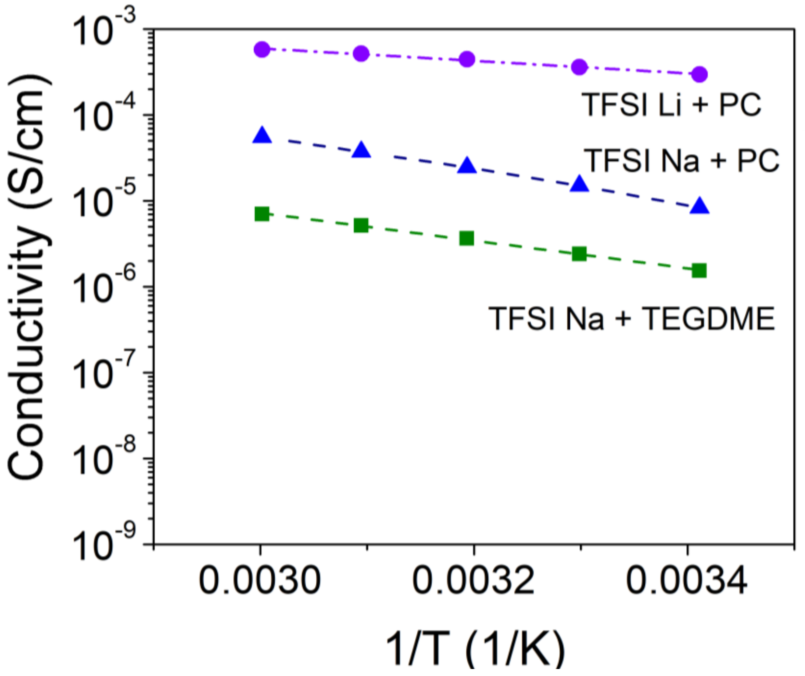


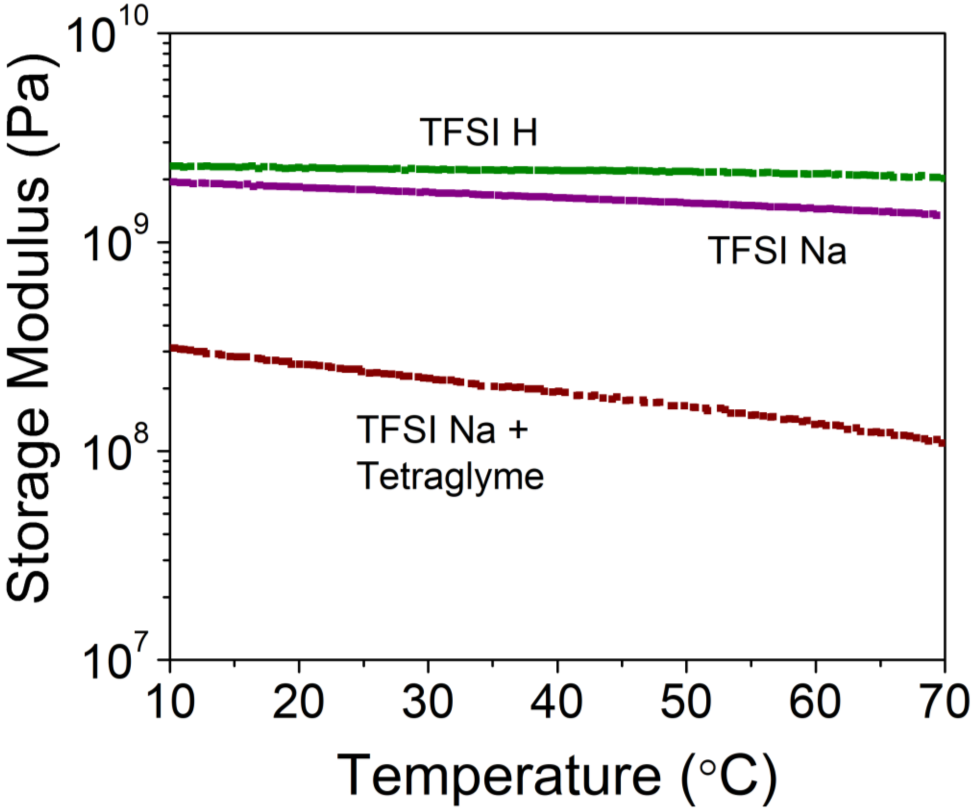
Approach and outcome

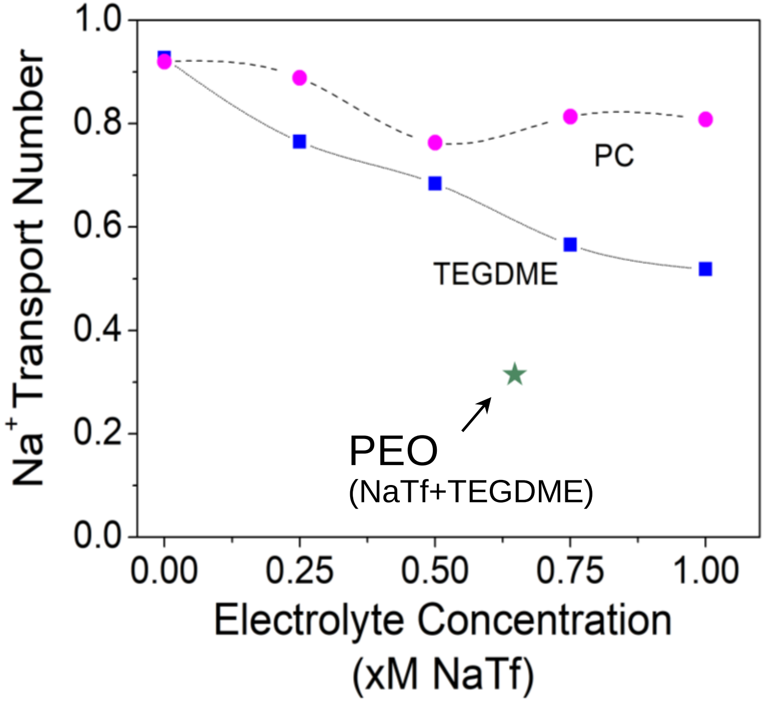
1. 3-step cation exchange process of a commercial proton-conducting membrane, Kraton Nexar ®
2. Membrane is ultra thin (20 µm) but mechanically robust

Lehmann, Nanda, Saito et al. (in preparation 2022)

Ultra-thin Na^+ conducting Nexar TFSI membranes (20 µm) are mechanically robust with high ionic conductivity. These membranes will be integrated into RFBs during FY22.







Key Findings:

1. High storage modulus (1.5 GPa for dry, 200 MPa after plasticizing)
2. High cation transport number
3. High Na^+ conductivity approaching 1 mS/cm at RT.

Key Accomplishments (FY21)

Sodium polysulfides (Na_2S_x) are a promising class of low-cost catholytes for nonaqueous RFBs

- Demonstrated lab-scale prototypes (ca. 20 mAh, 40 mWh) with outstanding cycling stability (250+ cycles)
- Precipitation of S and Na_2S_4 phases did not inhibit system reversibility
- Coulombic efficiencies of 100% within experimental error
- Use of BASE ceramic membrane limits system to low concentrations and current densities

Integration of AC impedance features enables quantification of ohmic vs. kinetic vs. transport overpotentials

- Impedance studies at open-circuit do not provide information about non-equilibrium behavior.
- Biphenyl/Na_2S_x RFB primarily limited by reaction kinetics at cathode

Na metal/Na_2S_8 hybrid flow cells were assembled using commercially available polymer membranes

- Nafion115 (Na^+ form) membrane exhibited low crossover rate for Na_2S_8 catholyte
- New polymer membranes are needed to enable higher current densities and longer cycle life

Nexar single-ion conducting membrane has promising properties for nonaqueous RFBs

- Demonstrated cation exchange method to reach high ion replacement ratio and ion-exchange capacity
- GPa storage modulus to ensure processibility and mechanical integrity during cell operation
- High ionic conductivity at room temperature and enhanced cation transport number (>0.8)
- Transport property tunable by solvents of different dielectric constant values

Ongoing and Future Work (FY22)

Nonaqueous Flow Batteries with single-ion conducting membranes

- Benchmark the performance of various polymer and ceramic membranes
    - **Targets**: ASR < 50 $\Omega\,cm^2$ with minimal crossover rates to enable balanced cell cycling for months/years
- Investigate how higher concentrations impact cell performance
- Perform technoeconomic analysis to compare cost and energy density of various nonaqueous chemistries.

Membrane-Free Flow Batteries with Na Metal Anodes + High Energy Catholyte

- Develop Na-based nonaqueous electrolytes which effectively passivate Na metal.
    - **Target**: thin, dense passive films comprised primarily of inorganic halide salts (e.g., NaF)
    - Inhibit Na dendrite growth and catholyte permeability
- Track passive film growth kinetics using AC impedance

Develop ion selective membranes for low-cost, high-capacity nonaqueous flow batteries

- **Targets**: tunable solvent uptake, thickness<20 µm, ionic conductivity > 10^{-3} S/cm, storage modulus > 100MPa, good (electro)chemical stability
- Investigate transport properties and cross-over using in operando FT-IR
- Perform technoeconomic analysis of the membrane development

Publications and Patents (FY21)

1. E. C. Self, J. L. Tyler, J. Nanda "Ambient Temperature Sodium Polysulfide Catholyte for Nonaqueous Redox Flow Batteries" *Journal of the Electrochemical Society*, **2021**, 168, 080540.
2. G. Yang, M. L. Lehmann, S. Zhao, B. Li, S. Ge, P. Cao, F. M. Delnick, A. P. Sokolov, T. Saito, and J. Nanda. "Anomalously high elastic modulus of a poly (ethylene oxide)-based composite electrolyte." *Energy Storage Materials* 35 (**2021**): 431-442.
3. X. Feng, H. Fang, P. Liu, N. Wu, E. Self, L. Yin, P. Wang, X. Li, P. Jena, J. Nanda, D. Mitlin "Heavily Tungsten Doped Sodium Thioantimonate Solid State Electrolytes with Exceptionally Low Activation Energy for Ionic Diffusion" *Angewandte Chemie International Edition* **2021** (In Press, DOI: 10.1002/anie.202110699).
4. Evaluation of electrochemical performance and redox activity of Fe in Ti doped layered P20-$Na_{0.67}$ $Mn_{0.5}$ $Fe_{0.5}$ O_2 cathode For sodium ion batteries, D. Darbar, N. Muralidharan, R. Hermann, J. Nanda, I. Bhattacharya, Electrochimica Acta 380, 138156, 2021.
5. Stable Potassium Metal Anodes with an All-Aluminum Current Collector through Improved Electrolyte Wetting, P. Liu, Y. Wang, H. Hao, S. Basu, X. Feng, Yixin Xu, J. A. Boscoboinik, J. Nanda, J. Watt, and D. Mitlin, Adv. Mater**.** 2020, 2002908
6. J. Nanda, F. M. Delnick, E. C. Self, "Sodium Polysulfide Based Catholyte for Ambient Temperature Non-Aqueous Redox Flow Batteries" ORNL Internal Invention Disclosure No. 81928777.
7. J. Nanda, G. Yang, T. Saito, F. M. Delnick, "Mechanically robust solid electrolyte composites for alkali and beyond alkali metal batteries" . U.S. non-provisional patent application No. 17/397,233, 2021.

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